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HYPERVALENT IODINE(III) PROMOTED RING-REARRANGEMENT AND ARYLATION STRATEGIES

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Abstract. The chemistry of hypervalent iodine(III) reagents have widely been explored in many organic transformations for the construction of C-C as well as C-N bonds especially for their environmentally benign behavior, low toxicity and milder reaction conditions. The synthetic usefulness of such reagents has been experienced in many ring transformations as well as arylation reactions due to their excellent yield of the products and selectivities.

In this present context, we have showed the role of HTIB and NaN3 in the ring contraction of rigid exocyclic-β-enaminones for the synthesis of cyanocyclopentanones and concurrent cyanation without direct use of cyanating agent under milder reaction conditions.[1] The prepared cyanocyclopentanones were then converted into ∂-valerolactam molecules by PIFA mediated ring expansion reactions with detailed mechanistic investigation.[2] The structure of the final ring contraction as well as expansion products were further established by single crystal XRD analysis.

On the other hand, The phenyliodine(III) diacetate in presence of K_2CO_3 in acetonitrile solvent has been found to be an excellent combination for the intermolecular N-arylative aromatization of exocyclic-β-enaminones for the synthesis of triarylaminophenols.[3] Wide range of symmetric as well as asymmetric triarylaminophenols were prepared under metal free reactions which complements the transition metal catalyzed N-arylation reactions. The regioselective intramolecular arylation of exocyclic-β-enaminones has also been achieved by the combination of HTIB and $AgSbF_6$ in dichloroethane solvent for the synthesis of carbazole and Imidazopyridine type of molecules in good to excellent yield.[4] The detailed mechanism of the C-C and C-N bond formation reaction has been established with spectroscopic evidences.

References

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